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Synthesis and Application of Magnetic Nanoadsorbent in Removal of Toxic Metals from Aqueous Solution

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ABSTRACT

Magnetic nano adsorbent is cost-effective and easily synthesized in the laboratory by chemical Co-precipitation method that provides not only high adsorption capacity but also rapid adsorption rate. The magnetic nano adsorbents were synthesized by Ferric and Ferrous ions precursor solution in the presence of ammonium hydroxide. In the present investigation, a magnetic nano adsorbent has been employed for the removal of Pb (II) from an aqueous solution by batch adsorption technique along with photocatalysis. The different parametric study also carried out such as initial concentration of Pb (II), adsorbent dose, contact time, and Solution pH. The Pb (II) was fast adsorption and the equilibrium was achieved within 45 minutes. The amount Pb (II) adsorbed increases as the temperature increase. The optimal pH for Pb (II) was around 5.4 and for the removal of Pb (II) ions was up to 96.00%.

The employed adsorbents were characterized by SEM, X-ray diffraction (XRD), Vibrating spinning magnetometer (VSM), and FTIR. The Kinetic of adsorption study was examined for the pseudo-first-order model and pseudo-second-order models. This Photocatalytic adsorption study obeys Pseudo second-order kinetic. The reusability and regeneration of magnetic nano adsorbents were studied and were recycled up to 87.00 %.

Keywords: *Ferric and Ferrous ions, Co-precipitation, Magnetic Nanoadsorbent, Adsorption, VSM, Photocatalysis, Kinetics.*

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INTRODUCTION

Municipal wastewater is the combination of liquid or water-carried wastes originating in the sanitary conveniences of dwellings, commercial or industrial facilities, and institutions, in addition to any groundwater, surface water, and stormwater that may be present. Untreated wastewater generally contains high levels of organic material, numerous pathogenic microorganisms, as well as nutrients and toxic compounds. These toxic metals could cause accumulative poisoning, cancer, and brain damage when found above tolerance levels [1]. The major sources containing lead are the wastewaters from process industries engaged in lead-acid batteries, paint, phosphate fertilizer, electronics, and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sea spray, etc. Due to the hazardous nature of Pb (II), it may directly or indirectly cause anemia, headache, chills, diarrhea, and poisoning leading to the dysfunction of kidneys, reproductive system, liver, brain, and central nervous system also [2]. Many industries such as electroplating,

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metal-processing, paint, plastics alloy, batteries, ammunition, the ceramic glass industries, etc. generate large quantities of wastewater containing various types and concentrations of heavy metals. Although many heavy metals are necessary for small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations. Heavy metal pollution is of greatest concern among the kinds of environmental pollution due to the high toxicity and mobility of heavy metals. It is well documented that lead is one of the industrial wastewater contaminants and its pollution exists in the wastewater of many industries [3]. Unlike most organic pollutants, heavy metals do not undergo biological degradation and tend to accumulate in the organisms, thereby eventually entering the food chains [4]. In recent years, magnetic nanoparticles have attracted much attention because of their unique magnetic properties and widespread application in different fields such as mineral separation, magnetic storage devices, catalysis, magnetic refrigeration system, heat transfer application in drug delivery systems, magnetic resonance imaging (MRI), cancer therapy, and magnetic cell separation [1–11].

The application of magnetite in the field of wastewater treatment is becoming an interesting area of research. Nanoparticles exhibit good adsorption efficiency especially due to higher surface area and greater active sites for interaction with metallic species and could easily be synthesized; several researchers have used it as an adsorbent [12–16]. However, effluents of different industries contain a higher concentration of nickel than its acceptable limit. Although nickel is an essential micronutrient for animals and takes part in the synthesis of vitamin B12, its higher concentration causes cancer of the lungs, nose, and bones and it may also cause nausea, rapid respiration, headache, cyanosis, and dry cough [17,18]; Therefore, it is necessary to treat industrial wastewater rich in Pb(II) before their discharge into the water bodies.

Many technologies such as ion exchange, reduction flocculation, membrane filtration, precipitation, electrochemical, filtration and reverse osmosis have been proposed by different scientific workers for the removal of nickel from aqueous solutions and effluents. However, most of these technologies require high operational and maintenance costs and also generate toxic sludge [19,20]. Due to high expense, these techniques are not suitable for small-scale industries, especially in developing countries. Adsorption is one of the most promising techniques for the removal of metallic pollutants from industrial effluents [21]. Adsorption offers high efficiency, cost-effectiveness, and easy handling among the majority of physiochemical treatment methods. Among the waste treatment procedures, adsorption techniques are the most widely used as low-cost alternative technology. Cheaper and effective adsorbents could be formed from abundant natural materials or certain waste materials (or products) from industrial and agricultural activities. In general, an adsorbent that requires little processing or is abundant in nature, or is a by-product or waste material from another industry is called a "low-cost" adsorbent [22].

In recent years, a vast number of publications have been dedicated to the removal of heavy metals from wastewater by using adsorption techniques with different low-cost materials, such as moss peat [23], coconut husk, a sugar industry waste [24], chitin [25], sawdust [26,27], green algae [28,29], fly ash [30], bone char [31], lignite [32], zeolite [33–35], wood [36], tea waste [37–40], etc. The biosorption potential of red mushroom biomass for Se (IV) ions from aqueous solutions using a technique batch biosorption [41-47].

The present experimental research aims to explore the utilization of magnetic nano adsorbent, which is cheap and easily synthesized in the laboratory. The nanosized structure of magnetic nano adsorbents shows high adsorption capacity because of the larger surface area. Overall magnetic nano adsorbents should have the good capability as metal removals from aqueous solution and industrial and sewage wastewater. This investigation is undertaken for the application and management of such magnetic nano adsorbents for useful purposes. Although there are many researchers and scientists who have been developed several techniques and concentrated on adsorptive removal by different kinds of adsorbents.

This Research article focuses on the synthesis of magnetic nano adsorbent by chemical co-precipitation method and its application ineffective removal of Pb(II) from synthetic aqueous solution with different parametric conditions.

MATERIALS AND METHODS

Chemicals

All chemicals and reagents are used in this experimental research are analytical grade and purchased from LOBA CHEMIE INDUSTRIES LTD, MUMBAI. The chemicals used in this study were lead nitrate, ferrous chloride, ferric chloride, ammonium hydroxide solution, ethyl alcohol, and dimethyl glyoxime.

Synthesis of Magnetic Nanoadsorbent

The precursor solution of ferrous and ferric salts was dissolved in 50ml of double distilled water at 298K in a round bottom flask with mechanical stirring on a magnetic stirrer (REMMI Motors Ltd. Mumbai) to form a transparent solution. Add ammonium hydroxide in the above clear solution dropwise, because every drop of Liq. ammonia makes the solution becomes turbid and colloidal, the magnetic particles are seen in the colloidal solution. The synthesis of magnetic nano adsorbent follows the chemical co-precipitation methods shown in the following chemical reaction.

$$FeCl_2 + 2FeCl_3 + 8NH_4OH \xrightarrow{358K} Fe_3O_4 + 4H_2O + 8NH_4Cl \quad (1)$$

The magnetic properties of synthesized magnetic particles were examined by taking a simple magnet nearby the R.B.F containing a colloidal solution of magnetic particle, it is seen that the colloidal particles attracted towards the magnet strongly, also which confirms the synthesized materials contain the magnetic properties shown in Fig.7. The Fe_3O_4 nanoparticles were then washed with distilled water and alcohol and dried at 55°C. The structure and morphology of the Fe_3O_4 nanoparticles were characterized by X-ray powder diffraction, XRD shows high-intensity Cu Kα radiation (λ = 1.54060 A) with the 2θ range from 20° to 80 °. The XRD and SEM study shows that the average size of synthesized magnetic nano adsorbent up to 22.33nm indicates the nanomaterials have high surface area.

Preparation of Pb(II) solution

The preparation of Lead nitrate obtained from LOBA CHEMIE INDUSTRIES LTD, MUMBAI was selected for this study as a source of Pb(II) ions. The Pb(II) stock solution was prepared by dissolving a specified weight of $Pb(NO_3)_2$ in 500mL of distilled water, and subsequently diluted to the required concentrations were used without further purifications.

Photocatalytic adsorption of Pb(II) onto magnetic nano adsorbents

For the photocatalytic removal of Pb(II) from the aqueous solution, the batch-adsorption techniques have been e performed by mixing magnetic nano adsorbents with Pb(II) aqueous solution. The 30 ml solution of the required concentration ranging from10-100 mg/L of Pb(II) was prepared from the stock solution and add 100mg of magnetic nano adsorbents into 100ml bororsyl beaker under U.V irradiation for photocatalytic treatment were carried out in presence of oxygen by low-pressure Hg vapor lamp wavelength range from 435-650 nm, 35 to 65 lumens/watt which provide UV-C irradiation which is very suitable for high band-gap photocatalytic nanomaterials. Photocatalytic reactors were assembled in the laboratory by purchasing all required parts from the market and as per the guideline of the Lelesil Innovative system. Before U.V irradiation 100 mg of adsorbent was added and stirred in the dark for 15 minutes so that adsorption equilibrium could be established. The solutions were then exposed to the U.V for irradiation with constant stirring throughout the experiment as shown in Fig.1. The Kinetics and equilibrium adsorption of Pb(II) ions onto the nano adsorbents were carried out at different temperatures, namely 25⁰, 35⁰, 45⁰. Then 30mL of Pb(II) aqueous solution with known initial concentration, Co (mg/L), ranging from 10 to 100 mg/L was added to100ml beaker then test solutions centrifuge at 300 rpm for 15 minutes. The equilibrium adsorption capacity, Qe, of Pb (II) aqueous was calculated using the mass balance, according to the following equation [41]

$$Qe = \frac{Co - Ce}{m} V \quad (2)$$

where V is the sample volume (L), m is the mass of magnetic nano adsorbents (g), Co is the initial concentration of Pb(II) in the solution (mg/L), and Ce is the equilibrium concentration of Pb(II) in the solution (mg/L). For time-dependent data, C replaces Ce and Q replaces Qe in Eq. (2).

Characterizations

RESULTS AND DISCUSSION

FTIR Analysis

The I.R spectra obtained by FTIR can help

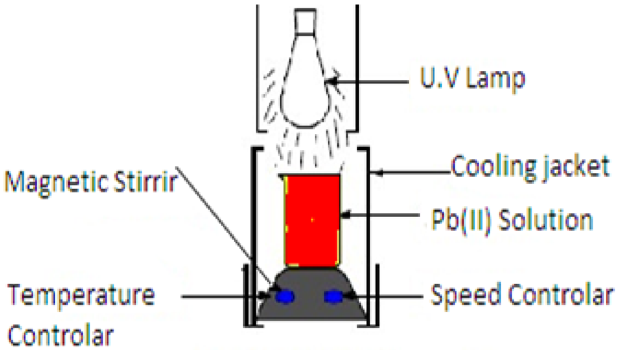

Fig 1. Showing schematic diagram of photocatalytic removal of Pb (II) by magnetic nano adsorbent

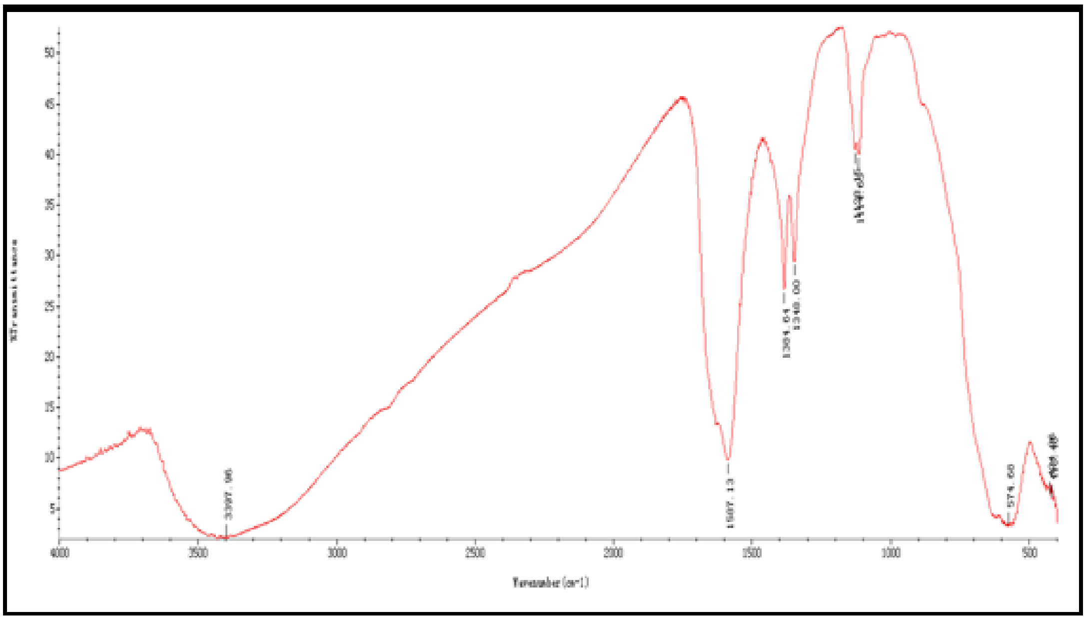

Fig.2. FTIR of magnetic Nanoadsorbent showing different I.R frequencies.

identify the different bond frequencies present in newly magnetic nano adsorbent The FTIR measurements were performed by using (Lambda Scientific FTIR-7600) with KBr background over a range of 4000-400 cm^{-1} to determine magnetic material. The FTIR provides structural information about the presence of certain functional groups in the unknown molecule. The frequencies at 587.0cm^{-1} and there is an obvious adsorbent band at a low-frequency zone of 500–700 cm^{-1}, which is assigned to the stretching vibration of the Fe–O bond in iron oxide A slight shift of Fe–O peak from 574.6cm^{-1} to 569 cm^{-1} displays that some of the metal ions are adsorbed onto the iron oxide nanoparticles. As shown in FTIR graph Fig.2. The characteristic absorption peak of magnetic fluid also appears at round 589 cm^{-1} the synthesized material is Fe_3O_4. The peak at 3390.77cm-1 is due to the presence of moisture in KBr and some small noised peaks are due to the presence of impurities in magnetic nanoparticles.

SEM Analysis

The SEM result obtained from interactions of an electron with a solid sample of nano adsorbent gives information about the nano adsorbent including surface and structural morphology whether nano adsorbent crystalline or amorphous, the composition of nano adsorbent, and orientation of nanomaterials making up the nano adsorbent. In

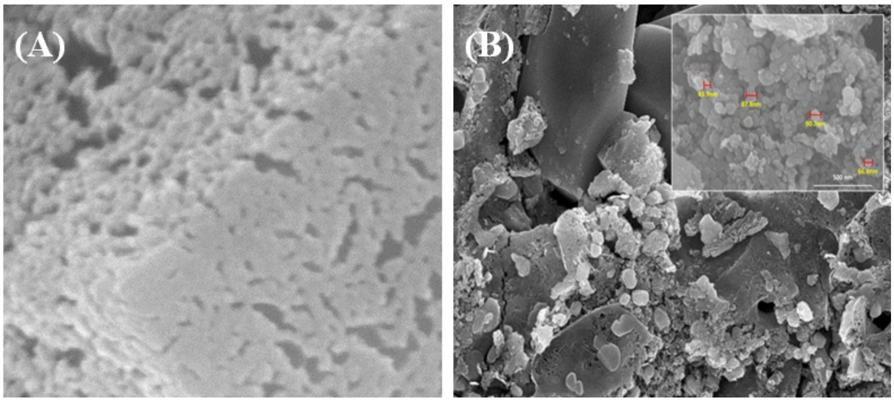

Fig.3. (A) Before treatment, (B) After treatment

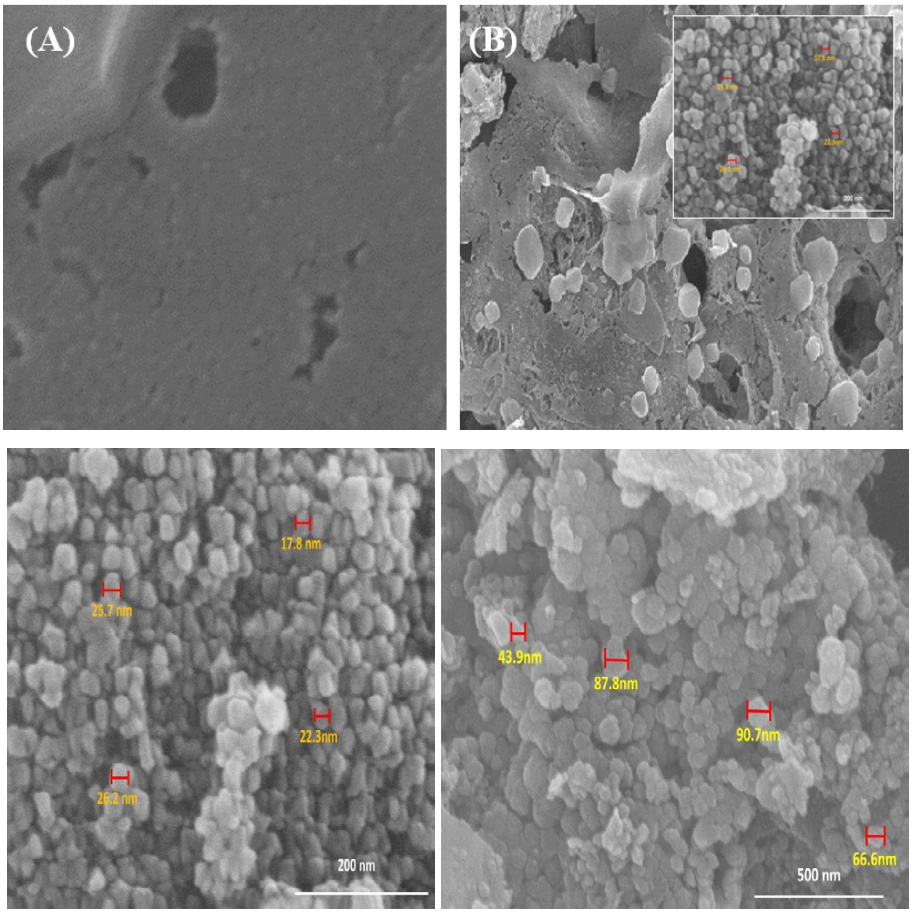

Fig.4. (A) Before treatment, (B) After treatment

this study the adsorbent material was analyzed on Ultrafine imaging Mag from 50000X to 100000X, EDS before and after treatment it shows the greater extent of adsorption of Pb(II) ions on magnetic nano adsorbent as shown in Fig.3.A) and Fig.4.A) and Fig.3.B) and Fig.4.B) respectively. In this research article the topographical evaluation of as-prepared magnetic nano absorbents before and after treatment has been confirmed by performing Scanning Electron Microscope (SEM) revealed in Figures. The SEM images of_magnetic nano adsorbents show distinct adsorption of Pb(II) ions

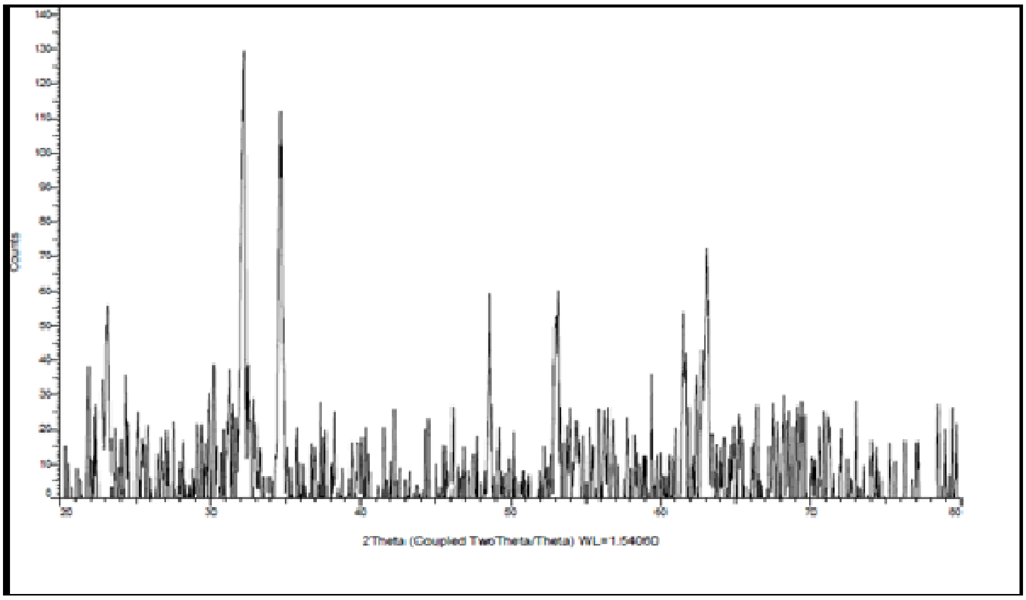

Fig.5. XRD pattern of Magnetic nano adsorbent

on the surface of the adsorbent. The Scanning Electron Microscope (SEM) allows us to image specimens at high magnifications using several different contrast mechanisms. Composition-based contrast is especially helpful when examining multi-component samples, such as cross-section samples prepared from multi-layer coatings/paints. The energy dispersive x-rays spectrometer allows the collection of qualitative and quantitative information about the elemental composition of spots and regions of interest. SEM is widely used to study the morphological feature and surface characteristics of adsorbent materials.

XRD Analysis

The X-ray diffraction patterns of the fabricated magnetic material are mentioned below. Differential peaks 2θ appeared at 27 º, 30 º, 35 º, 43 º,53 º,57 º,63 º, 74 º which are just the evidence of the existence of Fe_3O_4 Fig.5. Calculating the grain size according to Scherrer formula Eq.3, obtained 45.8 nm for the Fe_3O_4 nanoadsorbent. The diffraction peaks reveal a cubic spinel structure with no other phases existing in the sample. The selected area electron diffraction peaks corresponding to the (800), (400), (511), (422), (222), (311), (220), and (111) planes for Fe_3O_4 match with the XRD pattern.

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

VSM Analysis

A vibrating Spinning magnetometer (VSM) is used to determine the magnetic properties of the synthesized MNA as a function of an applied external magnetic (H). Fig. 6. shows the VSM curve of magnetic nano adsorbent. Based on the obtained VSM curve at room temperatures, the magnetic behavior of the MNA can be identified. For example, at room temperature, MNA shows a hysteric loop feature that indicates that the MNA is paramagnetic. Also, from the plateau part of the VSM curve, saturation magnetization (Ms) can be determined. In the present characterization most important that the MNA materials should possess sufficient magnetic for use in practical applications and it is very useful in the present study.

Effect of pH

It is well known that pH is one of the most important parameters which affect the adsorption process. This photocatalytic experimental study was performed to find out the optimum pH on the adsorption of Pb(II) ions onto the magnetic nano adsorbent using different initial pH values changing from 2 to 10 pH Fig.8 indicates that the influence of pH on the adsorption of Pb(II). As seen, the best condition of removal of Pb (II) ions is pH dependent with the highest adsorption at pH 5.4 and removal of Pb (II) ions up to 96.00%.

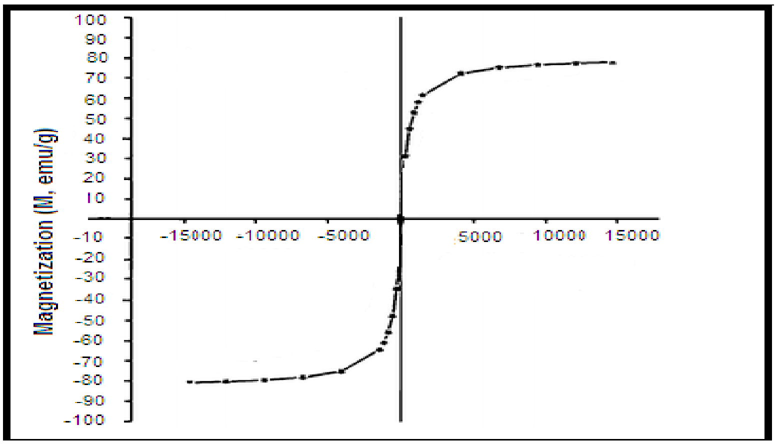

Fig.6. VSM curve of Magnetic Nanoadsorbent.

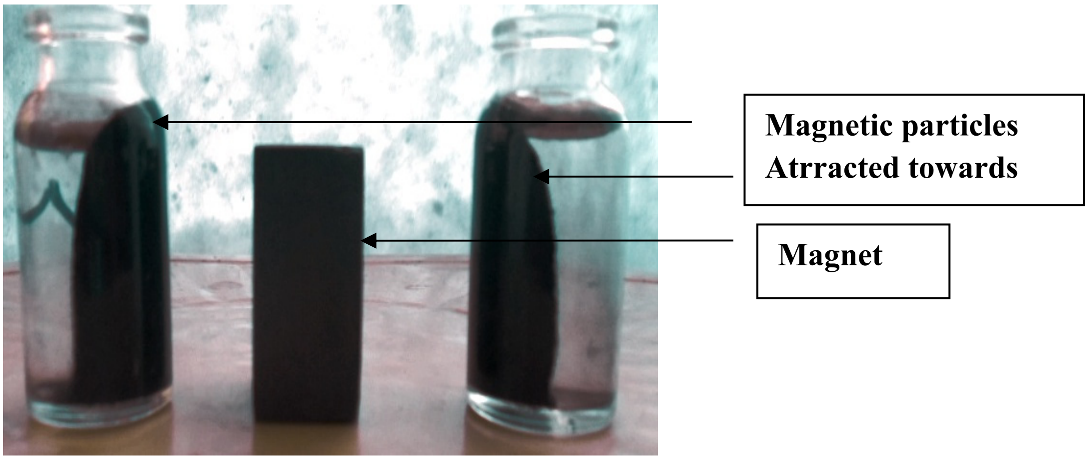

Fig.7. Photo image showing of magnetic nano adsorbent contains sufficient magnetic properties.

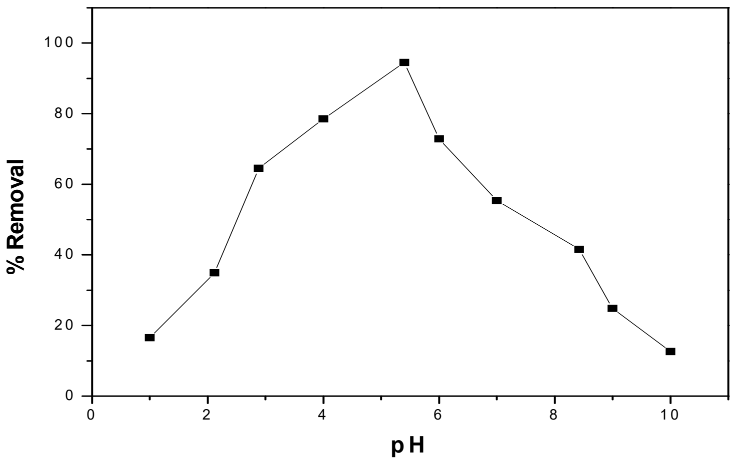

Fig.8. Effects of pH on Pb(II) ions removal.

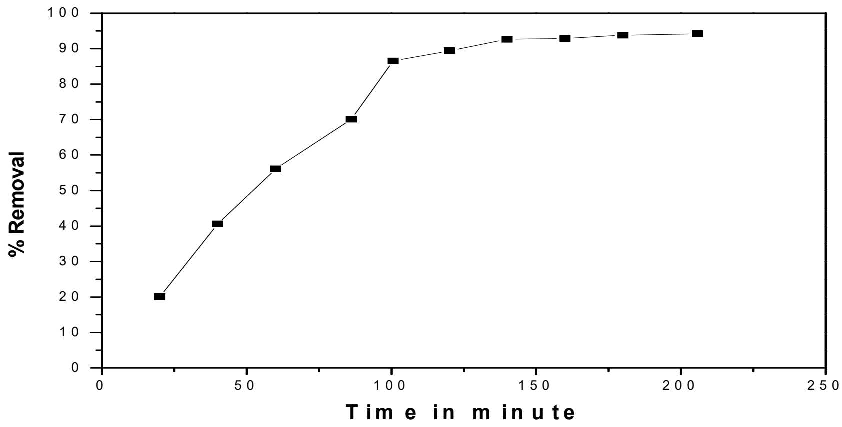

Fig.9. Effects of contact time on Pb(II) ions removal.

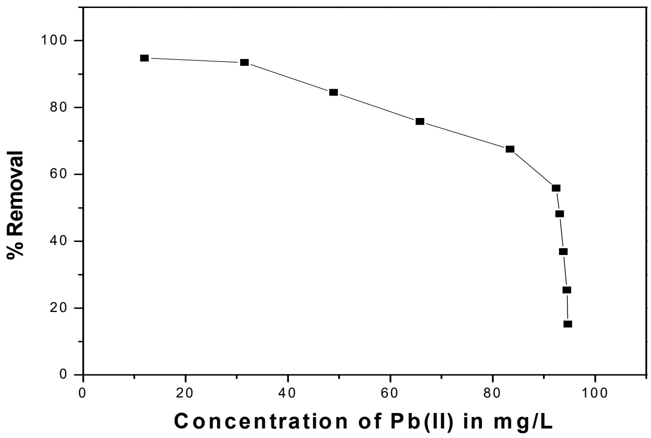

Fig.10. Effect of initial concentration of Pb(II) ions.

Effect of Contact Time

As the adsorption process proceeds, the sorbent reaches a saturation state. The adsorption capacity of sorbent decreases after the equilibrium was established. The adsorption rate was tested by performing a batch adsorption experiment. The magnetic nano adsorbent was kept in contact with Pb(II) ion solution for different periods at an interval of 25 minutes. The experimental data represented in Fig.9 shows that initially as the time increases percentage removal of Pb(II) ion also increases then after certain periods equilibrium gets established.

Effect of Initial concentration of Pb (II)

The adsorption capacity of magnetic nano adsorbents as a function of the initial concentration of the Pb(II) has been studied at different concentrations in batch adsorption experiments. The percentage removal of Pb(II) from aqueous solution decreases with an increase in the concentration of metal ions as shown in Fig.10. Initially, the percentage removal of Pb(II) ions increases 10 mg/L and 20mg/L after that removal efficiency get decreases due to the increase in the concentration of Pb(II) ions in the solution.

Effect of Adsorbent dose

Magnetic nano adsorbent has a great influence on the adsorption process and determine the potential of magnetic nano adsorbent due to the nanosize providing a large surface area for binding to remove metal ions at a specified initial concentration. The effect of the dose of magnetic nano adsorbent on Pb(II) ions removal is indicated in Fig.11. At equilibrium metal adsorption capacity decreases with an increase in adsorbent dose from 1 to 5 mg/L. This is because

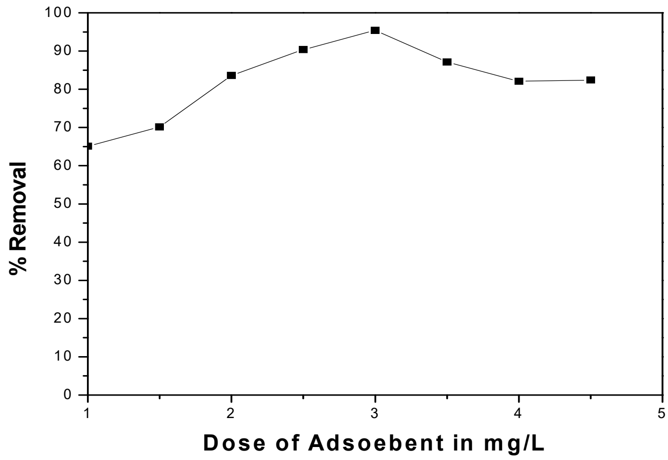

Fig.11. Effects of adsorbent dosage on Pb(II) ions removal.

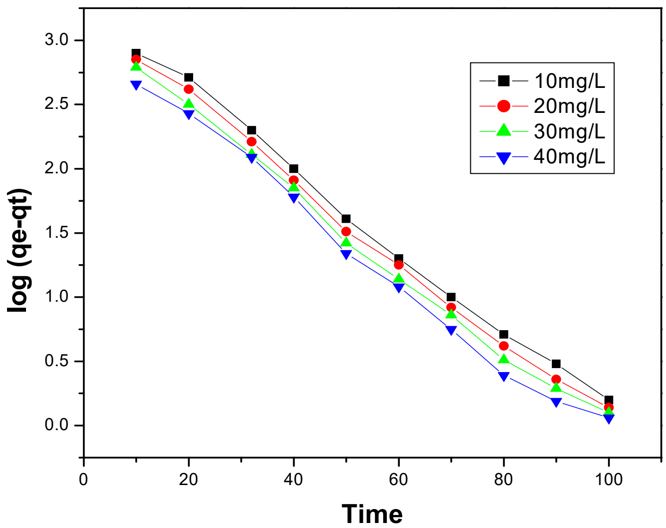

Fig.12. Pseudo First Order kinetics of Pb(II) metal ions Adsorption on magnetic nano adsorbent.

the decrease in percentage removal can be due to the concentration gradient between the sorbate and sorbent, an increase in the amount of magnetic nano adsorbent concentration causes a decrease in the amount of metal adsorbed onto the unit weight of the magnetic nano adsorbent.

ADSORPTION KINETICS

The kinetic study provides valuable information about the mechanism of adsorption and subsequent investigation of the controlling mechanism of the adsorption process as either mass transfer or chemical reaction in order to obtain the optimum operating conditions for industrial-scale batch processes [42]. The uptake of Pb(II) on magnetic Nano adsorbent is examined at different time intervals shows the effect of time on the uptake of Pb(II). In batch systems, adsorption kinetics is described by several models based on adsorption equilibrium such as the pseudo-first-order and the pseudo-second-order kinetic models. The linearized pseudo-first-order kinetic model takes the following form Eq.4 [43,44]:

$$q_{t=}q_e - q_e \exp(-K_1 t) \quad (4)$$

where qt and qe are the amounts of metal adsorbed at time t and equilibrium, respectively, and K_1 (min^{-1}) is the first-order reaction rate constant. The values of k_1 were calculated from plots of ln (qe-qt) Vs. t as shown in Fig.12.

The pseudo-second-order kinetic model

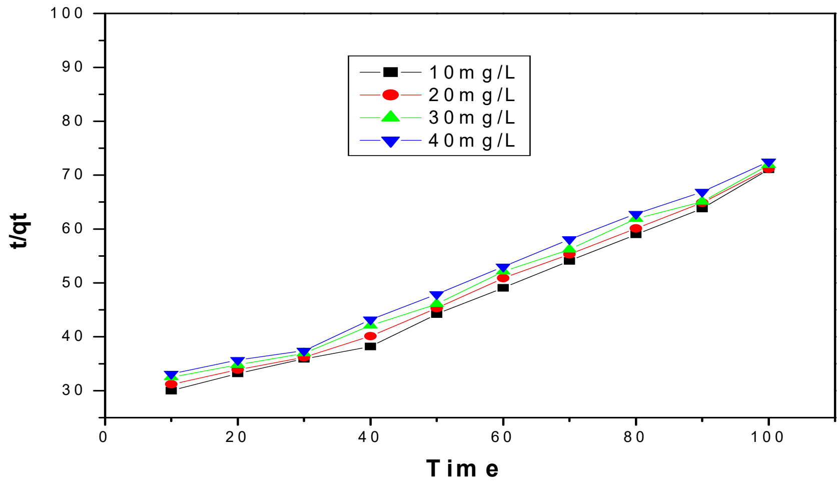

Fig.13.Pseudo-second-order kinetics for Adsorption of Pb(II) ions on magnetic Nanoadsorbent

Table No. 1

Adsorbent dose(g/L)	Initial Metal concentration in mg/L	Adsorbent	first order kinetics			
			q_e (exp)	K_1	q_e(cal)	r^2
1	10		3.5	0.02	4.7	0.96
3	20		3.2	0.03	4.6	0.95
Adsorbent dose(g/L)	Initial Metal concentration in mg/L	**Magnetic nanoadsorbnet**	**Pseudo second order**			
			q_e (exp)	K_2	q_e (cal)	r^2
1	10		3.8	0.74	3.46	0.99
3	20		3.7	0.72	3.67	0.99

considered in this study is given as shown in Eq.5. [43,44]. The values of K_2 were calculated from plots of t /qt Vs Time as shown in Fig.13.

$$t / q_t = 1/ K_2 qe^2 + t/qe \qquad (5)$$

where K_2 (gmg^{-1} min^{-1}) is the second-order reaction rate constant. The experimental data and the parameters of both models are tabulated in Table.1. It is obvious that the coefficient of correlation (R2: 0.99, 0.99) for the pseudo-second-order kinetic model is higher in comparison with the pseudo-first-order kinetic model (R2: 0.95, 0.96) and the calculated value of qe for the pseudo-second-order kinetic model is very close to the experimental value. Similar experimental results indicate that the pseudo-second-order kinetic model fits the equilibrium data for heavy metal ion sorption on magnetic nano adsorbent from aqueous solutions quite well [43,45,46].

Table No.1.

Comparison between adsorption rate constants, the estimated qe, and the coefficients of correlation associated with the Lagergren pseudo-first-order and the pseudo-second-order

Kinetic models at 25^0C.

REUSABILITY OF MAGNETIC NANOADDSORBNET

Recycled, Reuse and Regeneration studies of magnetic nano adsorbent is an important characteristic in the industrial sector. In this experimental research adsorption-desorption cycles of the magnetic nano adsorbent were performed two times, in order to maximize the desorption of palladium. For this reusability, 0.1 N Nitric acid was used. The results showed that the magnetic nano adsorbent a were recycled up to 87.00 %. This research study focus that the magnetic nano adsorbent being effectively recycled, reusable and stable.

CONCLUSION

The present investigation of photocatalytic experimental research examines Kinetic of adsorption for pseudo-first-order model and pseudo-second-order models, adsorption study obeys Pseudo second-order kinetic. The parametric study shows the removal of Pb(II) ions is pH dependent with the highest adsorption and optimum pH at 5.4. The magnetic nano adsorbent showed promising characteristics which can be used for the removal of heavy metals from industrial and sewage wastewater.

This method is particularly applicable for the treatment of low-volume industrial streams, where disposal of relatively large quantities of sludge generated, is still an economically competitive solution when compared to other treatment options; in particular hauling for off-site disposal of the entire wastewater stream. In such small-scale applications, the development and implementation of other treatment alternatives generating potentially lower amounts of residuals are frequently not justified due to cost. Treatment with magnetic nano adsorbent offers a robust option, capable of removing heavy metals to ppb levels from the complex matrix with metals present in various forms such as dissolved, colloidal, emulsified, and particulate.

The magnetic nano adsorbent with an average particle size of 22.33nm was synthesized using a chemical co-precipitation method. This nano adsorbent was successfully examined for the removal of Pb(II) metals from synthetic aqueous solutions. Also, the results showed that the magnetic nano adsorbent a were recycled up to 87.00 %.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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